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Laser Isotope Separation of Carbon by Multiple IR Photon and Subsequent UV Excitation of CF_3I Molecules

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Abstract. A new approach to laser isotope separation is considered. It is based on collisionless multiple photon ir laser excitation and subsequent uv laser dissociation of vibrationally excited molecules. TEA CO_2 and excimer XeF, XeCl lasers are used for ir excitation and uv dissociation, respectively. The products of photolysis (C_2F_6) are enriched with ^{12}C.

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Among a variety of approaches to the problem of laser isotope separation [1, 2] the two-step selective dissociation of molecules through an excited electronic state [3, 4] and the collisionless multiple photon dissociation of complex molecules by ir laser pulses [5] are of considerable interest.

The main disadvantage of the first approach is a relatively small spectral shift of the uv absorption band for the vibrationally-excited $v=1$ ground state molecules and hence insufficient selectivity of the process as a whole. For the second approach, extremely high ir laser power densities (typically in excess of 10^7 W/cm^2) are needed for attaining a reasonable dissociation yield. The selectivity of isotope separation at a high laser power density is relatively low due to considerable line broadening in a laser field, and other factors.

In the present paper a new approach to laser isotope separation free from the above-mentioned disadvantages is considered. The approach is based on multiple photon ir laser excitation at a moderate laser power density and subsequent uv laser dissociation of vibrationally excited molecules. Isotope separation of carbon is carried out by this method. In our earlier work [6] photoisomerization of trans-dichloroethylene was carried out by using an analogous excitation scheme.

Experiment and Results

The multiplephoton excitation of CF_3I was carried out by using a TEA CO_2-laser (Fig. 1) on the $R(14)$ line of 9.6 μm band.

This laser line is near the maximum of the multiple-photon absorption peak of CF_3I [7] (in the vicinity of the Q-branch centre of the symmetrical vibration ν_1 (^{12}C-F)). The laser pulse energy and duration were 0.8 J and 70 ns. The XeCl ($\lambda=308$ nm), XeF ($\lambda=350$ nm) excimer lasers and N_2 ($\lambda=337$ nm) laser were used

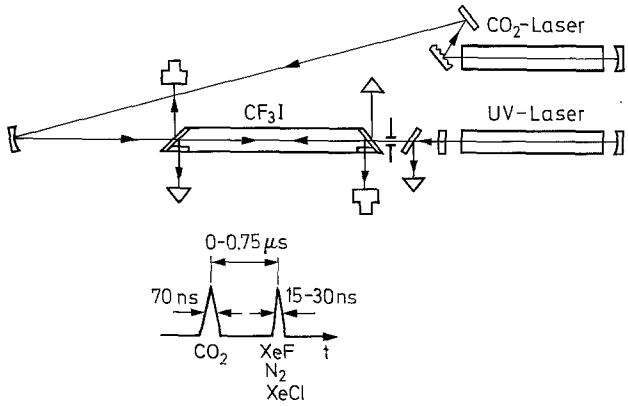

Fig. 1. Experimental set-up. ▽-coaxial photoelement, ⊓-thermopile. The lower diagram gives the time sequence of ir and uv laser pulses

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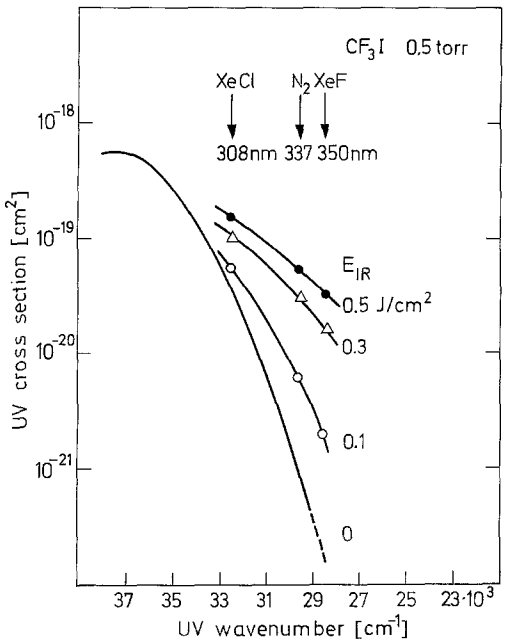

Fig. 2. The long-wavelength edge of the CF_3I uv absorption band at various ir laser power densities. The CO_2 laser line $R(14)$ at 9.4 μm

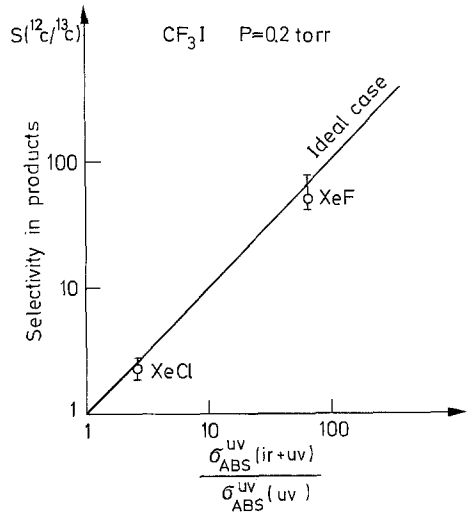

Fig. 3. The selectivity of the ir-uv dissociation process of CF_3I molecules in dependence on the ratio $\sigma(\mathrm{ir}+\mathrm{uv})/\sigma(\mathrm{uv})$ of the uv absorption cross section of ir-laser excited molecules to the uv absorption cross section of unexcited molecules. (Circles denote experimental selectivity data obtained with XeCl and XeF excimer lasers at a CO_2 laser energy density of 0.24 J/cm^2. For XeF laser the measurements give a lower estimate for the selectivity $S \geqq 48$)

as an uv source of radiation. For excimer lasers laser pulse energy and duration were 50 mJ and 30 ns, and for N_2-laser 3 mJ and 15 ns.

The uv laser pulse had a delay of 0–750 ns relative to the CO_2 laser pulse. The quantitative measurements of the CF_3I decrease and the analysis of the final output products were carried out by using an ir spectrometer.

The isotopic selectivity was measured by a mass-spectrometer at the *m/e* ratios of 119 and 120 of the $C_2F_5^+$ fragment. Selectivity was determined at a CF_3I pressure of 0.2 Torr and at the CO_2 laser power density of 0.24 J/cm^2. No essential dissociation yield was registered at such a power density without uv irradiation.

The uv absorption measurements were carried out in a 0.92 m absorption cell at the CO_2 laser power density of up to 0.7 J/cm^2 and at a gas pressure of 0.1–1 Torr.

Discussion

Absorption at the used uv laser frequencies is strongly increased for vibrationally-excited molecules. Figure 2 shows the long-wavelength edge of the CF_3I electronic absorption band for excited molecules at various ir laser power densities and also, for comparison, for unexcited molecules. The largest increase of the cross section takes place at the wavelength of the XeF laser.

Excitation of the CF_3I molecule on first electronically excited state leads to the dissociation into the CF_3 radical and atomic iodine in the excited state $^2P_{1/2}$ with a quantum yield of about 1 [8]

$$CF_3I \xrightarrow{h\nu_{uv}} CF_3 + I(^2P_{1/2}).$$

The final products are C_2F_6 and I_2

$$CF_3 + CF_3 \rightarrow C_2F_6, \quad I + I \rightarrow I_2.$$

Thus, when $^{12}CF_3I$ molecules are excited selectively by ir radiation and then, after uv laser excitation, dissociation of the molecules takes place, the photolysis product C_2F_6 will be enriched with ^{12}C.

The enrichment coefficient was determined experimentally according to

$$\beta = \frac{[^{12}C/^{13}C]_f}{[^{12}C/^{13}C]_i}.$$

At low "burning" (decrease of molecular concentration due to laser irradiation), the parameter β coincides with the selectivity value. On the other hand, the selectivity of dissociation is approximately equal to the ratio of the uv absorption cross sections with and without ir excitation,

$$S = \frac{\sigma_{abs}^{uv}(\mathrm{ir}+\mathrm{uv})}{\sigma_{abs}^{uv}(\mathrm{uv})}.$$

This can be compared with experimental data (Fig. 3). As can be seen from this figure, the measured selectivity values of the dissociation process correlate well with the relative increases of the uv absorption cross section.

The method of isotope separation which was described above is of practical value for relatively heavy isotopes

in case when there are no powerful lasers for ir excitation of molecules at the specific frequencies.

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